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Twenty-fifth day of February 2000

K. Ward

KAY WARD
<u>TEAM LEADER EXAMINATION</u>
<u>SUPPORT AND SALES</u>

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PROVISIONAL SPECIFICATION

Invention Title: Conductive and Flame Retardant Plastic Fillers

Applicant: Contract Research & Development (M) Sdn. Bhd. & David John Tadgell

The invention is described in the following statement:

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CONDUCTIVE AND FLAME RETARDANT PLASTIC FILLERS

TECHNICAL FIELD

This invention relates to the use of a filler derived from rice husk in plastics to enhance the conductivity and flame retardant properties of the composite plastics. The invention has particular but not exclusive application to the following families of plastics:-

1. Thermoplastic Resins
2. Thermoset Plastics
3. Rubbers and Elastomeric Materials
4. Conductive Coatings and Printing Inks

BACKGROUND ART

Composite plastics are well known. Fillers are usually added to plastics to save cost or to enhance a particular mechanical property or other characteristics of the plastics. The usage of fillers is usually accompanied by coupling agents that enhance the polymer-filler and filler-filler interaction so that the expected properties are realised. The present invention is concerned with fillers which enhance the conductivity and flame retardant property of plastics. Such plastics have wide application in the aeronautical, mining, computer, rubber and polyurethane industries among others. For example, it is often desirable to prevent the build up of static charges which can cause sparks (and hence explosions or electrical damage) or production problems, eg. collection of dust and poor feeding of materials through machinery. More highly conductive plastics can also be used for Electro Magnetic Interference shielding, for example.

Carbon black fillers, aluminium flakes and fibres, stainless steel fibres and chopped carbon fibres have all been used as fillers for the purpose of rendering composite plastic conductive. Likewise other chemicals such as Halogen compounds or Triethyl Phosphate have been used to achieve the flame retardant property.

A number of theories have been proposed to explain how discreet particle fillers impart conductivity and flame retardant properties in composite plastics.

In order for current to flow in a conductive polymer compound, electrons must travel along the filler as the plastic itself is an excellent insulator. To achieve this flow the discreet particles of the filler must be in contact or separate by a minimum distance which is probably less than 100 Angstroms. There are three properties of the filler particles which will effect the average inter-particle distance for a given filler loading in a polymer system. These are particle size, shape (structure), and porosity. Smaller size, irregular shape and high porosity all result in smaller inter-particle distances and hence higher conductivity. A fourth property of the particle which is relevant to conductivity and flame retardant properties in the composite plastics is surface chemistry, that is the presence of oxygen on the surface. The presence of appreciable quantities of oxygen on the surface (called volatile content) acts as insulation and hence reduces conductivity.

The known conductive fillers such as carbon black, aluminium, stainless steel and carbon fibres are expensive and furthermore some of these materials have other processing difficulties, eg. Aluminium fibres and stainless steel fibres settle in liquid environments due to their high density. Further problems with known conductive fillers are that they often compromise other properties of composite plastics such as flame retardance and strength.

Static electrification of articles can lead to a number of undesirable effects including:

- Attraction of dust particles.
- Attraction between surfaces, e.g. plastic films and textile yarns.
- Risk of fire or explosion caused by sparking near inflammable liquids, gases, and explosive dusts, e.g. coal dust and flour.
- Risk of shock to persons handling equipment.

The accumulation of electrostatic charges can be prevented by using materials of low resistance. The resistivity of natural rubber can be lowered by compounding with suitable ingredients. Alternatively, as static electrification is a surface phenomenon, the product can be covered with a conducting surface layer.

Low resistance rubber is required for a wide range of applications, such as rollers for textile machinery, conveyor belting, fuel hoses, flooring, footwear, cables, equipment used in hospital operating theatres, and aircraft components.

The terms "antistatic" and "conductive" are restricted here to rubber products rather than the rubber itself because the electrical resistance of the product depends not only on the resistivity of the rubber but also on the shape and most probable positions of charge generation and discharge.

Natural rubber is normally considered to be an electrically insulating material but it can be an electrically insulating material but it can be compounded to give electrical resistivity lying anywhere between 1 ohm/cm. and 10^{15} ohm/cm. The most common means of reducing resistance is to add a suitable carbon black (super conductive furnace). Resistance falls with a decrease in particle size, increase in black "structure" and increase in concentration. For light coloured products certain grades of aluminium silicate may be used as antistatic fillers although these are usually less effective in reducing resistance than the super conductive furnace. There are also other proprietary antistatic agents that are available, such as ethylene oxide, but still these agents are less effective then the super conductive furnace.

The applicant has found that rice husk (more preferably but not exclusively carbonised rice husk) is particularly suited for use as a filler in plastics as it has been found to enhance the conductivity and flame retardant properties of the composite plastics. The presence of appreciable quantities of oxygen on the surface of carbonised rise husk acts as insulation for each aggregate, thereby reducing the conductivity and also reducing the flammability.

Typical chemical and physical properties of fresh and carbonised rice husk are detailed as follows:

- consists of 20-23% of paddy
- husk burning: 20% ash by weight
  90-95% is silica (amorphous and crystalline)
- physical characteristics: bulk density 96.12-112.14 kg/m^3
- pH 7.14 (husk ash)
- moisture content 5.6-7.2%, dry basis
- ash 22.2%

Chemical Composition

Moisture Content	: 5.6-7.2%, dry basis
Ash:	: 22.2%
Protein	: 2.4%
Crude fat	: 0.7%
Carbohydrate	: 32.0%

	Fresh RH	**Carbonised RH**
Al_2O_3	0.025%	0.023%
CaO	0.36%	0.12%
NaO	0.034%	0.018%
SiO_2	96.2%	53.88%
Fe_2O_3	0.041%	0.022%
MgO	0.16%	0.078%
K_2O	0.69%	0.95%
P_2O_5	0.57%	0.27%

It is an object according to one aspect of the present invention to provide an alternative filler which will enhance the conductivity and flame retardant properties in composite plastics. The filler is desirably cheap and does not compromise other characteristics of the composite plastics including flame retardant, strength and above all the filler is from a vegetable-based origin, which makes it an environmentally friendly filler.

SUMMARY OF INVENTION

The present invention in one aspect resides in the use of a carbonised vegetable-based filler to provide improved conductive and flame retardant properties in composite plastics.

Preferably, the carbonised vegetable-based filler is carbonised rice husk.

Preferably, the carbonised rice husk is burnt at about 800°C for about 4 seconds. Most preferably, the carbonised rice husk is burnt at 803-804°C for 3-4 seconds.

In another aspect the invention resides in a composite plastics including a vegetable-based filler when used as a conductive or flame retardant article.

Preferably, the carbonised vegetable-based filler is carbonised rice husk which has been burnt at 803-804°C for 3-4 seconds.

The present invention also exhibits the usage of fresh and carbonised rice husk as a blowing agent when used in combination with recycled (reclaimed) and or virgin natural rubber. Though other conventional blowing agents have been used with natural or synthetic rubber to achieve the similar products but so far no blowing agents have been used with recycle (reclaim) rubber to produce similar products. Further more the conventional blowing agents are expensive. When rice husk is used at different dosages the blooming effect is different. It was also noted that the rice husk does not only work as a blowing agent, but also as a plasticizer and a filler. The properties achieved are comparable to conventional blowing agents, when using fresh or carbonised rice, has no difference to the conventional blowing agent other then the colour of the end product.

Ebonite, a hard, dark-coloured plastic-like material, is the reaction product of rubber and a large proportion of sulphur. Simple rubber / sulphur mixtures are seldom used in practice; they suffer from poor processability, require long cure times and lead to excessive shrinkage and heat evolution during cure. Accelerators, fillers, processing aids and other compounding ingredients are widely used in ebonite, as in soft rubber vulcanised rubber, to ease processing, shorten cure times and modify properties. The curing times for ebonite are generally up to ten (10) hours at 150° C, thus making ebonite products expensive. Ebonite can be made from synthetic, such as BR, NBR, SBR and Nitrile rubber and as well as from Natural rubber. High strength, low thermal conductivity, chemical resistance and insulating properties of natural rubber make it a popular choice. Although it has been superseded in many applications by synthetic thermoplastic and thermosets, it is still used for outstanding chemical resistance and electrical properties coupled with high mechanical strength and ease of machining.

The present invention exhibits the usage of fresh and carbonised rice as an accelerator when used in combination with recycled (devulcanised) or virgin natural rubber, and at the same time making ebonite a conductive product when carbonised rice husk is used. Though other conventional accelerators have been used with natural or synthetic rubber (virgin or recycled) to achieve the similar products but so far no accelerators like the rice husk material has been used with recycled (devulcanised) rubber to produce similar products. Further more the

conventional accelerators and conductive carbon black are expensive and difficult to blend and process. When rice husk is used singularly at different dosages the activation effect is different to meet industrial requirements. Generally for ebonite production the sulphur content should be in the range of 26-40phr. Accelerators are less effective in ebonite than in soft rubber and large quantities are generally required. Basic accelerators such as guanidines and aldehyde-amines are preferred. Inorganic activators such as magnesium oxide, magnesium carbonate and lime are also effective when used with organic accelerators to reduce cure time without the risk of over heating.

Common inorganic fillers used in ebonite are china clay, talc, silica, whiting and magnesium oxide. These also reduce shrinkage and heat evolution but loaded ebonite generally have weaker mechanical properties than unloaded ones. Carbon black does not reinforce ebonite and is normally only added for pigmentation, although conductive carbon black are sometimes used to prepare electrically conducting ebonite.

BEST MODE

Following is an example of the invention, in this example the filler is carbonised rice husk (CRH) which has been burnt at 803-804°C for 3-4 seconds. After this the CRH is obtained.

The manner in which the rice husk is burnt is believed to be important in achieving the desired surface area, surface structure and porosity necessary for conductivity and flame retardant properties in the composite plastics to be achieved. At this stage the range of temperature and the duration of the time of burning which achieves the desired result has not been fully explored, however it is predicted that the temperature range will be from about 100-950°C and the time range will be from about 2-30 seconds, although these ranges may be much narrower. The importance of controlled burning in a prescribed time results in obtaining better surface area and porosity which in turn offers ideal properties emitting anti-static, flame retardant and enhancing physical properties of the material. In the absence of controlled burning, the surface area, surface structure and porosity would be distorted. While the present exemplification involves use of carbonised rice husk it is possible that the desired results may be achieved by use of other carbonised vegetable-based fillers.

EXAMPLE 1

A thermoset application called pulforming was used to manufacture fibre reinforced bolts. Fibre glass tows (36 tow of 8000 tex) are pulled into a resin bath that contains:

1. Polyester and Vinyl Ester combination, ie. 60% Vinyl Ester (Derakane 411 - Dow Chemical) and 40% Polyester (Everpol 3260 AR - P.T. Arinde).
2. Zinc Sterate (mould releasing agent) - 1.18% of the resin volume BYK 980 (improves wetting and dispersing of fillers in glass fibre reinforcement compounds) - 1.5% of the filler volume.
4. BYK 515 (air releasing agent) - 0.5% of the total volume of the resin mixture.
5. BYK 996 (wetting and dispersing additive for mineral fillers in hot curing, glass fibre reinforced UP-resin systems) - 2% of the resin volume.
6. Fillers (CaCO & Carbonised Rice Husk @ 55% & 12% of the resin volume).
7. Aluminium Trihydrate (2.4% of the resin volume).
8. Catalyst TBB - 2.12% of the resin volume.
   TBT - 0.53% of the resin volume.

The wet fibre glass tow is pulled into the mould and compressed at a pressure of 800psl (5600kPa) for 3.8 minutes at 130°C. Then the bolt is pulled out of the mould and left to cure.

The following day tests were carried out on the bolt with the following results:

Tensile strength at the thread - 50kN

Torque - 45ft/lb

Bond strength - BS 1610:Part 1, Grade 1.0

Fire rating - BS 5865:1980 - Persistence flame shall be less than 10 seconds

Electrical conductivity - less than 10 to the power of 9 Ohms.

EXAMPLE 2

All chemicals used are taken by percentage of weight of rubber. The rubber and the chemicals are mixed in a Banbury, for 5 minutes. Recycled rubber (reclaim) (220g) is first milled with zinc oxide (4.5%) - accelerator, which is followed with stearic acid (1.8%) - activator, Mercadibenzothiazole disulphide (MBTS)(0.5%), Tetramethylthiuram disulphide (TMTD)(0.2%)- accelerator, fresh rice husk (27%)-blowing agent and filler and sulphur (2.7%)- vulcanisate. Then the mixed compound is milled for five (5) minutes to form a sheet that is ready for curing. Then a piece of the sheet weighing about 32g is placed in a mould that it is to be cured for two (2) minutes in a oven at 150°C temperature. The conventional curing time is six (6) minutes at the same temperature of 150°C.

The rubber and the chemicals are mixed in a Banbury, for 5 minutes. The similar approach has been done for using SBR Rubber (100g), silica (62g), Peg 1500 (2.5g), Paraffin oil (5g), Zinc oxide (2.5g), Wing stay (0.5g), Wax (1g), Mercadibenzothiazole disulphide (MBTS) (1.5g), Tetramethylthiuram disulphide (TMTD) (0.2g), Stearic acid (1.5g) and Sulphur (2g). The milling was done for ten (10) minutes and later cured in the oven for six (6) minutes at 150°C.

This exercise was repeated by using fifty (50) percent of the virgin material compound and fifty (50) percent recycled (reclaimed) material compound, and cured in the oven at 150°C for two (2) minutes.

With the level, of rice husk dosage, the blooming effect can be controlled to suit the industries requirement.

Machine Operating Conditions

Virgin Rubber:

Mix properties; White filled mix	
Mooney viscosity, MLI + 3, 100°C	24
Mooney viscosity, MLI + 3, 120°C	18.5
Mooney scorch, t_5 MLI + 3, 120°C min	5.8
Monsanto Rheometer, 160°C	
time to 95% cross-linking, s	110

Recycle (Reclaim) Rubber

Mix properties Rice husk filled mix

By using rice husk the Mooney viscosity was lower then the conventional filler or blowing agent, thus lowering scotch and curing time respectively. As such this leads to a cheaper production system. Presently various fillers and blowing agents are being used in the production of soft/spongy rubber that would produce different types of cell structures for an end product, but the cost determines the market.

EXAMPLE 3

All chemicals used are taken by percentage of weight of rubber. The rubber and the chemicals are mixed in a Banbury, for six (6) minutes. The recycle (devulcanised) rubber is first milled with magnesium oxide (2%) - accelerator, which is followed with Diphenylguanidine (2%) - accelerator, fresh rice husk (30%) - accelerator and filler and sulphur (30%) - vulcanisate. After the milling at the Banbury for ten (10) minutes, it is then milled into a sheet. The mould was heated in the oven press to 150°C then the sheeted rubber is placed in the mould and it is cured for twelve (12) minutes. The conventional curing time is between eight to ten hours at the same temperature of 150°C.

A conventional formula for ebonite was selected to compare. The rubber and the chemicals are mixed in a Banbury, for 5 minutes. The similar mixing as above was followed, using SBR 5 Rubber (100g), ebonite dust (100g), China clay (50g), Magnesium oxide (5g), Dihenylguanidine (3g), Linseed oil (5g) and Sulphur (45g). The milling was done for ten (10) minutes and later cured in the oven for eight (8) hours at 150°C.

Mix properties; Rice Husk filled mix

Mooney viscosity, MLI + 3, 100°C	24
Mooney viscosity, MLI + 3, 120°C	18.5
Mooney scorch, t_5, MLI + 3, 120°C min.	5.8
Monsanto Rheometer, 160°C	
time to 95% cross-linking, s	110

By using rice husk the curing time is reduced tremendously twelve minutes as compared to eight to ten hours. The sulphur content in the rubber polymer is reduced by fifteen percent.

It will of course be realised that whilst the above has been given by way of an illustrative example of this invention, all such and other modifications and variations hereto, as would be apparent to persons skilled in the art, are deemed to fall within the broad scope and ambit of this invention as herein set forth.

Throughout the description and claims of the specification the word "comprise" and variations of the word, such as "comprising" and "comprises", is not intended to exclude other additives, components, integers or steps.

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PHILLIPS ORMONDE & FITZPATRICK

Attorneys for:

CONTRACT RESEARCH AND DEVELOPMENT (M) SDN. BHD. & DAVID JOHN TADGELL

David B Fitzpatrick